

Electric field-assisted formation of percolated silver nanolayers inside glass

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Abstract: A combination of direct current (d.c.) electric field and moderately elevated temperature is applied to a glass with embedded spherical silver nanoparticles in the near surface region. The field-assisted dissolution of silver nanoparticles leads to the formation of a layer of percolated silver clusters with modified optical properties beneath the glass surface. The distance between this produced buried layer and the surface of the sample can be controlled by the magnitude of the applied voltage. The same holds for the interferential colors observable in reflection. The presented technique is easy to implement and paves a route towards the engineering of the optical properties of metal-doped nanocomposite glasses via modification of the spatial distribution of metallic inclusions.

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OCIS Codes: (160.2750) Glass and other amorphous materials; (160.4670) Optical materials

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1. Introduction

Lately composite materials containing metal nanoparticles have found an increasing number of applications in different fields of science and technology [1-3]. In particular glasses containing metallic nanoparticles are of great interest for the field of photonics because of their unique linear and nonlinear optical properties, which are determined by surface plasma oscillations of the metal clusters. The surface plasmon (SP) resonance depends strongly on shape, distribution and concentration of the nanoparticles, as well as on the surrounding dielectric matrix. This offers the opportunity to manufacture very promising new nonlinear materials, nanodevices and optical elements by manipulation of the nanostructural properties of the composite medium. Recently, laser-based techniques leading to modifications of shape and arrangement of the metal clusters have increasingly become of great interest and proved to provide a very powerful and flexible tool to control and optimize the linear and nonlinear optical properties of such materials [4-7]. However, very recently we were able to show that there is a technologically simpler (and thus probably economically more attractive) technique to properly structure nanoparticles or modify their spatial distribution, and hence their optical properties: by applying a combination of an intense d.c. electric field and moderately elevated temperature silver nanoparticles embedded in glass matrix can be destroyed and dissolved in form of silver ions [8], resulting finally in optical transparency in the regions under the electrode. The phenomenon was physically interpreted in terms of ionization of the metal nanoclusters followed by the removal of ions from the clusters and their drift in the depth of the glass substrate. In this letter we demonstrate that, using the technique described in Ref. [8], conditions can be selected for which a buried layer of percolated silver clusters is formed several hundred nanometers below the glass surface, giving rise to almost arbitrary colors observable in reflection due to light interference. More generally, this technique allows the engineering of the optical properties of the material via gaining control over the spatial distribution of silver in the glass.

2. Experimental

The samples used in our experiments were prepared from soda-lime float glass by Ag-Na ion exchange and subsequent annealing in H_2 reduction atmosphere [9]. This technique results in the formation of spherical silver nanoparticles of 30-40 nm mean diameter in a thin surface layer of approximately 6 μm thickness. Single-sided samples were used in our experiments, made by removing a sufficiently thick layer from one side of the samples by etching in 12% HF acid. The volume filling factor of Ag nanoparticles ($f = V_{\text{metal}}/V_{\text{total}}$), estimated from scanning electron microscopy (SEM), is maximal near to the sample surface ($f \approx 0.7$) and decreases in the depth, dropping to zero within a few microns (Fig. 1). The electric-field assisted dissolution of Ag nanoparticles, as described in detail in Ref. [8], was performed by pressing two rectangular electrodes (7mm $\times$ 9mm in size) on the sample surfaces, the anode facing the layer containing nanoparticles. Then the sample was heated to a temperature of $\sim 250^\circ C$, and a d.c. voltage was applied. For the main results presented in this work, the voltage was increased in steps of 0.2 kV to a maximum value of 1 kV within a total time of 50 min, keeping the current below 200 μA at any time; finally the voltage was switched off and the temperature was reduced down to ambient temperature. This approach, which is similar to the one used for poling soda-lime glasses, was necessary to avoid dielectric breakdown of the material [10,11].

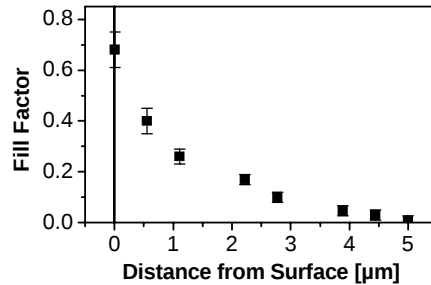


Fig. 1. Volume fill factor of silver in the nanocomposite samples, as obtained from SEM examination.

3. Results and discussion

The experimental procedure described above leads to nearly complete bleaching of the area under the anode. As an example, Fig. 2 gives microscopic pictures of a bleached sample; the two pictures, presenting exactly the same sample area (where a corner of the anode was placed, the electrode edge approximately 100μm inside of the ring labeled '1'), were recorded in reflection (Fig. 2(a)) and transmission mode (Fig. 2(b)) of the microscope, respectively. In reflection mode the border region around the electrode exhibits a rainbow-like pattern consisting of a sequence of several blue, green and red rings. In transmission mode (Fig. 2(b)), following the same path from untreated (location O) to treated area (location 6) of the sample, no rainbow pattern is observed, but only a gradual change of color from dark brown to faint yellow. The latter colors can be understood by the SP absorption of the silver nanoparticles being present in the sample initially, and their destruction by the dissolution process, governed by the strength of the electric field which quite obviously decreases with increasing distance from the anode edge. The remaining light yellow color within the bleached area indicates that a small amount of silver nanoparticles remains non-dissolved in the depth of the sample where the filling factor of nanoparticles is very low. This incomplete bleaching, as already observed in previous experiments [8], is due to the limited voltage of 1 kV applied here.

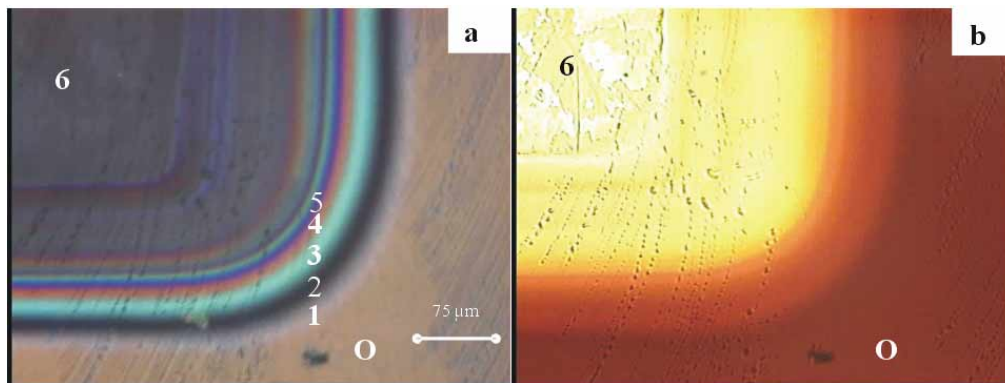


Fig. 2. Photographs of the segment of the anodic surface of silver nanoparticles containing glass sample after treatment at 1kV, 250°C. Photographs were taken using a microscope spectrophotometer [MPM 800 D/UV, Zeiss] equipped with CCD camera in: (a) reflection and (b) transmission mode. Numbers (2-5) refer to locations where reflection spectra were measured (see Fig. 3).

To get an idea about the physical origin of the rainbow pattern we recorded reflection spectra at different positions within the border region using a microscope spectrophotometer [MPM 800 D/UV, Zeiss], using a rectangular diaphragm of 1μm×10μm. The results are

shown in Fig. 3, where the individual spectra are labeled along with the numbering of the locations as shown in Fig. 2: at position 2 (in the first, dark blue ring) there is rather high reflectivity of $R \approx 22\%$ at 380 nm wavelength, but quite low reflectivity throughout most of the visible range; in contrast, the broad green ring (no. 3) exhibits a broad band of high reflectivity with a peak of $R \approx 24\%$ at 521 nm. The color of the next, red ring (no. 4) is obviously determined by the broad band of reflectivity around 633 nm with $R_{\max} \approx 23\%$, and finally the bright blue ring (no. 5) is characterized by the band around 459 nm with maximum reflectivity of $R \approx 17\%$. The most reasonable explanation for these spectra (and the whole rainbow pattern) is to assume that, during the dissolution process, an interface with considerable reflectivity in a variable (D.C. field-dependent) depth of typically a few hundreds of nanometers has been produced. Then wavelength-dependent constructive or destructive interference between the light reflected at this layer and the light reflected at the sample surface would be the source of reflection spectra, and the different colors would be due to different depths of this layer.

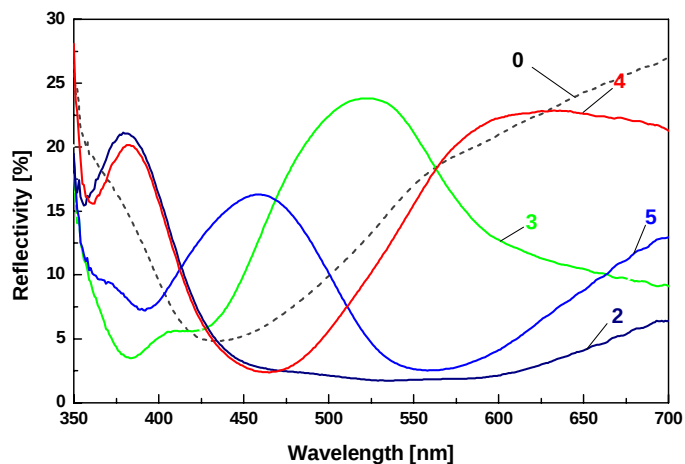


Fig. 3. Reflection spectra measured at different locations on the sample surface using a microscope spectrophotometer [MPM 800 D/UV, Zeiss]. The reflection spectra are numbered according to different locations shown in fig. 2a. For more information refer to the text.

We performed a very simple check of the plausibility of this assumption: if the colors are due to interference, the rainbow pattern must change dramatically when the phase change by π upon reflection at the sample surface is cancelled by a highly refractive contact liquid dispersed on the sample surface. And in fact, a thin film of CH_2I_2 ($n = 1.74$) provided such a complete change of the colors observed (not shown here, compare Fig. 5), whereas a thin film of water ($n = 1.33$) did nearly not change the pattern at all, only its brightness decreases considerably. The latter is compatible with the decreased reflectivity at the interface sample – liquid, as compared to the interface sample – air.

So the idea of interference appears to be correct, and we have to clarify the nature of the ‘interferometer’. In particular the following question has to be answered: which type of reflective layer is being produced during the electric field and heat treatment? For this purpose we studied the nanostructural changes in the samples using SEM. Figure 4 shows the border region between modified (left-hand side) and unmodified (right-hand side) regions of a sample which was cleaved along a line crossing these regions; note the different length scales of top view (Fig. 4(a)) and side view (Fig. 4(b)). For both pictures the SEM signal refers to an electron penetration depth of ~ 100 nm, and silver particles appear as white spots.

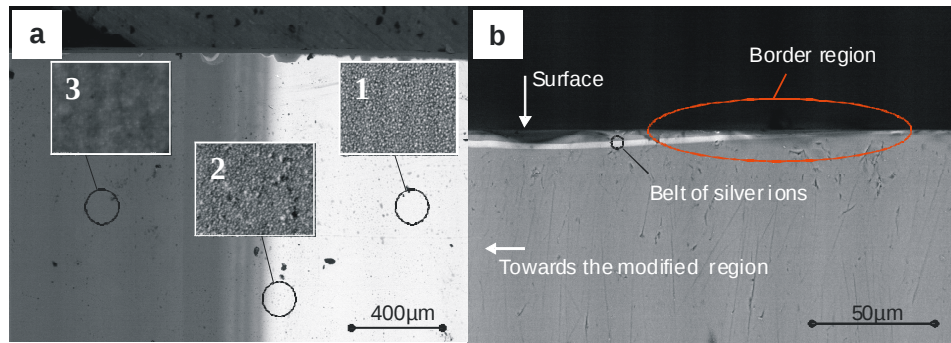


Fig. 4. (a) SEM picture of the surface of the sample taken in back scattered electron (BSE) regime (top view). Insets 1, 2 and 3 refer to locations in untreated region (location O in Fig. 2a), border region (location 1 in Fig. 2a) and modified region (location 6 in Fig. 2a), respectively. (b) SEM picture of the cross section of the sample.

In the top view of Fig. 4a and the insets, which were taken at higher magnification, it is clearly seen that the originally very high concentration of silver nanoparticles close to the surface (inset (1)) starts to decrease in the very border region (inset (2)), until in the bleached area no remaining silver nanoparticles can be identified any more (inset (3)). The side view in Fig. 4(b) shows that in the treated area the nanoparticles were destroyed not only in the near surface region, but in the depth of the sample as well. Moreover, a shiny belt can be observed at a depth of approximately 5 μm from the surface, the distance of this belt to the surface decreasing towards the border region. Silver ions, which were ejected from the nanoparticles during the dissolution process and drifted away in the depth, are at the origin of this belt, which could act as a buried reflective layer because of the depth gradient of ion concentration. Simple considerations, however, show that silver ions can not account for the reflectivity which are needed to explain the rainbow pattern: considering two-beam interference between the direct surface reflex (reflectivity R_1) and the reflex from the internal interface (reflectivity R_2), the maximum reflectivity is approximately (transmission losses neglected because of $R_1 \ll 1$) given by

$$R_I = 1/2 \cdot (R_1 + R_2 + 2\sqrt{R_1 R_2}). \quad (1)$$

Since the sample surface and the nearby region are depleted from silver after the treatment, it will be transparent having a refractive index similar to that of the original glass ($n \approx 1.5$), i.e., $R_1 \leq 0.05$. Thus, in order to achieve $R_I \approx 0.25$, as observed in the reflection spectra (Fig. 3), the interface to the buried layer must provide a reflectivity of $R_2 > 0.2$. If just Ag ions should provide this effect, only a refractive index change due to the UV absorption (at 265nm) of the ions could be the origin of reflection. In this case Fresnel's formulae require a refractive index difference of $\Delta n \geq 1.2$ to be generated by the ions' UV resonance. But the pertinent absorption cross section is too low: at reasonable concentrations of e.g. 0.35 wt-% Ag ions give rise to a peak absorption coefficient (at 265nm) of $\alpha \approx 50 \text{ cm}^{-1}$ [12]; the latter corresponds to a refractive index change due to this resonance of $\Delta n \leq 10^{-4}$. So, even at unrealistically high silver ion concentrations of 10 wt-% we are far away from the refractive index change needed.

Figure 5 gives the definitive proof of the interferential origin of the observed phenomena and exhibits the nature of the buried reflective layer: in the central part of the microscope pictures of the original rainbow area (left, narrow part) and of the same region after the removal of a number of very thin surface layers by etching of the sample in 12% HF acid are shown. Clearly the rainbow pattern has changed dramatically due to the removal of surface layers. At the position indicated by white circles (green ring, location 3 in Fig. 2(a)) the sample was carefully examined by SEM before etching and after each etching step. At an

etched depth of approximately 400nm a layer containing densely-packed percolated silver islands was observed (Fig. 5(a)). Etching of a slightly deeper layer revealed that the silver filling factor is still very high in the depth (Fig. 5(b)). For comparison Fig. 5(c) shows the SEM picture taken from the very surface of the examined green region before etching, demonstrating again that the Ag particles close to the surface have been completely destroyed there. Over all, it is an obvious conclusion that this buried layer of densely-packed percolated silver clusters provides the reflectivity needed to observe, via interference, the rainbow colors in the border region.

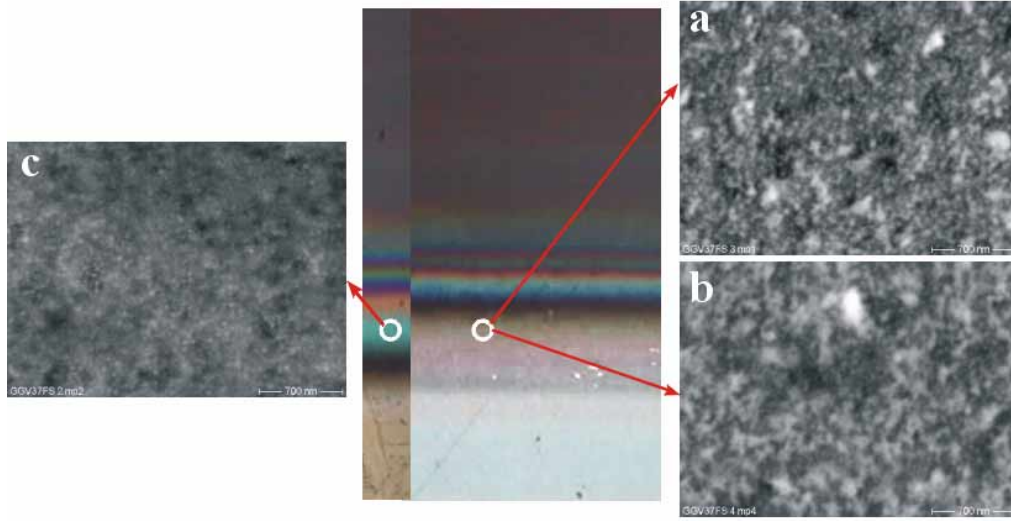


Fig. 5. SEM pictures taken from the location of the first green ring (location 3 in Fig. 2(a)). Pictures a and b were taken after successive etching of the sample surface up to depths of approximately 400nm. Picture c is presented for comparison and shows the surface of the sample before etching. The picture in the middle shows a segment of the border region of the sample before and after etching.

Since, to the best of our knowledge, there is no closed description for the optical properties of percolated silver films up to now, we will restrict the discussion in this letter to a plausibility check of the interface reflectivity. Roughly spoken, percolated silver films represent an intermediate state between the limits (i) isolated nanoparticles and (ii) compact metallic film. The latter has, in case of silver, high reflectivity ($R > 95\%$) throughout the visible range, caused by a very low refractive index ($n \approx 0.05$) and strong absorption. Owing to the pertinent low penetration depth of typically 10 nm, silver films can be described by their bulk properties – e.g., maximum reflectivity – already for film thickness of ≈ 20 nm and above [13]. The optical properties of isolated metal nanoparticles, representing the other limit, can often, up to quite high metal content, reasonably well be described using Maxwell-Garnett theory [2,7,14,15], which gives an explicit expression for the effective dielectric function $\epsilon_{\text{eff}}(\omega)$ of a composite material with spherical metal clusters of (volume) filling factor $f = V_{\text{metal}}/V_{\text{total}}$:

$$\epsilon_{\text{eff}}(\omega) = \epsilon_h \frac{(\epsilon_i + 2\epsilon_h) + 2f(\epsilon_i - \epsilon_h)}{(\epsilon_i + 2\epsilon_h) - f(\epsilon_i - \epsilon_h)}, \quad \text{with} \quad \epsilon_i(\omega) = \epsilon_b + 1 - \frac{\omega_p^2}{\omega^2 + i\gamma\omega}. \quad (2)$$

$\epsilon_i(\omega)$ and ϵ_h are the complex dielectric constants of the metal and of the surrounding matrix, respectively. For $\epsilon_i(\omega)$ the Drude model was used, where γ is the damping constant of the electron oscillations, ϵ_b is the core electron dielectric function, and the free electron plasma

frequency is given by $\omega_p^2 = Ne^2/m\epsilon_0$ (with N : density of free electrons, and m : electron effective mass). Based on this description, the complex refractive index of a composite medium with dielectric constant $\epsilon_{eff}(\omega)$ can be expressed as

$$n_{eff}(\omega) = \sqrt{\epsilon_{eff}(\omega)} \quad (3)$$

Using Eqs. (2) and (3) and the parameters $\epsilon_h = 2.3$, $\omega_p = 9.2$ eV, $\gamma = 0.5$ eV, $\epsilon_b = 4.2$, (all taken from Ref. [7]), the optical constants $n(\omega)$, $k(\omega)$ of glass with spherical Ag nanoparticles were calculated as a function of the volume filling factor of metal clusters in the glass matrix. Finally, Fresnel's formulae were applied to determine the reflectivity of an interface of the nanocomposite to the pure transparent matrix material (here glass with $n = 1.5$) was calculated. The results of the calculation are shown in Fig. 6 with f (volume filling factor) as the only parameter.

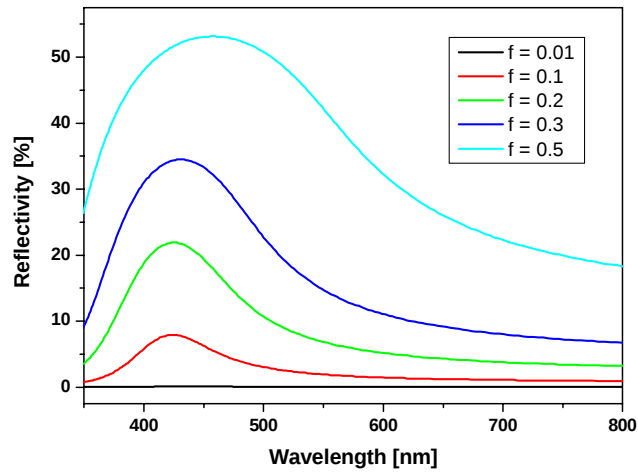


Fig. 6. Calculated reflectivity for interface between Maxwell-Garnett silver in glass nanocomposite and neat glass, with fill factor f as parameter

As it can easily be seen, there is a strong dependence of reflectivity on the Ag filling factor, which influences both the real and imaginary parts of the effective refractive index of Maxwell-Garnett composite glass. At low filling factor ($f \leq 10^{-2}$) the reflectivity is negligible ($R_{max} \approx 10^{-3}$), and only at quite high filling factor of $f \approx 0.5$ the required reflectivity $R \geq 20\%$ is achieved throughout the visible range. However at such high filling factors the Maxwell Garnett model is no longer a very accurate description of the optical properties, in particular not for the case of beginning percolation as observed for the buried layers in this work. So it makes no real sense to try to simulate the observed interference spectra on the basis of this simple model, although some qualitative agreement can be achieved assuming depths of 100 to 400 nm for the buried layer. On the other hand these simple considerations allow us to draw the important conclusion that already a rather thin layer of only a few tens of nanometers with high silver content (of the order of 50%) will definitely be able to provide the reflectivity needed to explain the reflection spectra observed by interference.

Thus, based on our observations we believe that the buried layer close to the border region is created due to the following mechanism: the combination of d.c. electric field and

temperature at first induces destruction of silver nanoparticles at the upper layer close to the surface of the sample. Further treatment, i.e., increase of the applied voltage, results in the drift of silver cations in the depth of the sample, and simultaneously electrons are attracted towards the anode, in the opposite direction of the cation movement. So at some depth the electrons may neutralize the cations again, thereby increasing the silver concentration there, which can lead to percolation and production of a layer containing densely-packed percolated silver clusters. The threshold of the dissolution process depends strongly on the filling factor of the nanoclusters [8]. Thus, the magnitude of the voltage applied to a sample with a gradient of the nanoparticle filling factor defines the distance between the surface and the buried layer of percolated silver clusters. This layer, finally, acquires a reflectivity that is high enough to observe interference of light reflected at the sample surface and at the buried layer. Since, in the border region the applied electric field – and thus the depth of this reflective layer – is non-uniform, rainbow-like patterns can be observed there.

At this point the obvious question occurs if similar experiments are possible, where the experimental parameters electric field, temperature and processing time are chosen so that a larger homogeneous area of interference is produced, and hence a uniformly colored region. For this purpose we conducted some preliminary experiments where d.c. voltages of 200 V, 400 V, and 600 V were applied at $\sim 250^\circ\text{C}$ in one step, for a total time of 30 min; electrodes with an area of $1\text{ mm} \times 2\text{ mm}$ were used. Due to imperfect contact not the whole regions under the electrode were colored homogeneously, but at least areas with dimensions of several $100\text{ }\mu\text{m}$ were produced which appear predominately in blue, green and red. In Fig. 7 two pictures show the edges of blue and red regions produced.

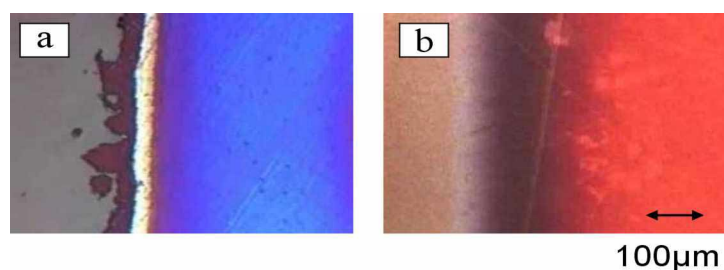


Fig. 7. Preliminary results showing large-area coloration through electric-field-assisted production of a buried percolated silver layer; processing at (a) 200V and (b) 600 V.

In summary, at first by applying an intense d.c. electric field at 250°C to a glass containing silver nanoparticles in a thin surface layer of a few microns, we managed to produce a buried layer of percolated silver clusters with modified optical properties. The buried layer was located in the border region between the treated and untreated regions of the sample. Reflection of light from the buried layer and its interference with the light reflected from the surface of the glass is believed to be responsible for the observed rainbow-like pattern.

Scaling of this technique via varying the applied voltage resulted in production of large areas which show homogeneous colors in reflection. In each case the distance between the produced buried layer and the surface of the sample was strongly dependent on the magnitude of the d.c. electric field applied. Once again reflection of light from the buried layer and its interference with the light reflected from the surface of the glass is believed to be responsible for the observed spectra in each case. Further thorough studies of the threshold and intermediate conditions as well as dynamics of the process are needed; this will be a subject of future work. What is clear, however, is the potential offered by this simple technique to produce, based on metal-doped nanocomposite glasses, devices with a need for wavelength selection.

Acknowledgments

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